Thermal oxydation during extrusion of polyolefins

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Abstract

The thermal oxidation during extrusion of polyethylene was studied under inert gas (nitrogen and CO_2) and compared with extrusion under air atmosphere. A strong reduction of degradation rate was found by optical observation and by infrared analyses. A mechanism for the change of color is proposed.

1. Introduction

The thermo-oxidative degradation of polyolefins during extrusion process produces dark particules in the polymer matrix incompatible with the quality of final products. It is the main cause of extrusion stop for cleaning the machine and is known to result from the contact of molten polymer with oxygen [1]. The degradation rate can be reduced using an inert gas inside the extruder in order to check the oxidative origin of the degradation. A modification of the extruder and a protocol are applied to collect and analyze the decomposed polymer in a critical zone, at the entrance of the die exit. Image analysis of the number and size of collected particles inside the polymer and the local infrared analysis inside these particles are able to directly connect the polymer browning to the number of carbonyl groups. The nature of chromophore was searched using quantum mechanics model to predict the UV-visible spectrum.

2. Experimental device and procedure

Two LDPE resins were extruded: 1003FE23 (Atofina) (MFI=0.3g/10min) and Lupolen 3721C (Basell) (MFI=0.1g/10min). 1003FE23 has little additives and no antioxidant, whereas Lupolen 3721C contains 1500 ppm of antioxidants (phosphates 1000 ppm and Irganox 1010 500 ppm). A laboratory single screw extruder Haake, with a 25:1 L/D ratio (50 mm screw diameter) in line with a capillary die, was modified to inert the feed hopper with either nitrogen or CO_2. Different extrusion conditions were applied: extrusion temperature from 220 to 280°C, flow-rate from 8 to 64 rpm, pressure from 105 to 270 bars. The different pressures were obtained with a set of capillaries with different length/diameter ratios. The samples are collected at this die-entry after 8 hours of extrusion under inert gas and in usual condition with extrusion under air. This location was recognized to be critical, the polymer remain for a long time in this stagnation zone. This zone acts as a reservoir of degraded particles which are after that relaxed as defects in the final extruded product. The samples were pressed to a 90µm thickness and analysed with visilog image analysis software on RGB components from scanned images. The number and the size of particles were deduced from each experiment in order to obtain a size distribution. The chemical composition of significant particles was analyzed with an infrared microscope (Nicolet 510P with an x15 lens on an analytical microscope) on surfaces down to 15x15 µm. The sample is embedded between KBr plates with nujol and the carbonyl bands were preferentially analyzed.

3. Experimental results

A strong reduction of the number of particles and of their size result from extrusion under inert gas (nitrogen, CO_2) (Fig.1). The number and the mean size of the particles are significantly lower under inert atmosphere compared with extrusion under air. The difference between the two polyethylenes is very weak for the number or the size of particles whatever is the extrusion condition. The content of antioxidant doesn't act on the No significant difference was notice between these two gases. The degradation strongly increases with extrusion temperature under air while it remains almost constant under inert gas. No significant difference was observed as a function of flow-rate or pressure. The image analysis exhibits an increase of browning with the size of the particles; the larger particles are the darker and browner.

The atmosphere in the feed-hopper controls the degradation near the exit of the extruder. There is no direct connection between these zones. The only way for the transit of gas is the molten polymer, which implies a dissolution and a diffusion of gas in the molten polymer. Under static condition nitrogen and CO_2 follow the Henry's law, the solubility of gas increases with pressure [2]. The general mechanism for the transport of gas is known but we don't have observed a significant variation of degradation content with the extrusion pressure.

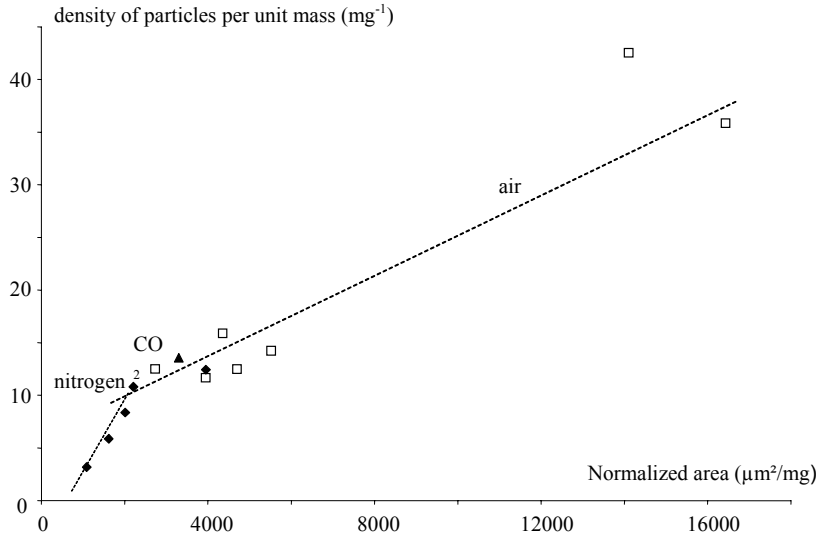

Figure 1 – Evolution of the normalized number of degraded particles as a function of their quantity under different atmospheres: air, nitrogen, CO_2

It is necessary to check the chemical origin of the appearance of these brown particles. The infrared analysis of the particles formed in different extrusion conditions shows various carbonyl groups between 1550 and 1850 cm^{-1}. The browner particles have the stronger infrared absorption groups. The various peaks were separated in individual components and interpreted using literature. A very strong correlation was found with the intensity of two coupled bands: 1620 and 1768 cm^{-1} which are enol bands. The enol form results from equilibrium with ketone form. The ketone form or other carbonyl groups doesn't produce any absorption in the visible optical range, there is no chromophore associated. We have check the possible chromophore nature of enol form. The β conjugated ketoenol, known to be a more stable form of enol, was studied by quantum mechanics. This method is able to predict the UV-visible spectrum from a description of the chemical structure. The CAChe software was used with the semi-empirical method MP5. The UV-visible spectrum exhibits a band at 400 nm which explain the red color of oxidized particles. The intensity of this band increases strongly with the conjugation of ketoenol groups. The Infrared spectra were also calculated and correspond precisely to the experimental data.

4. Conclusion

The effect of atmosphere is very efficient on polymer degradation, much more than antioxidant. A mechanism of action is proposed with an explanation of the link between oxidation and browning of particles.

References

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